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Removal and Recovery of Brilliant Green and Brilliant Yellow using Mesoporous Aluminophosphate Molecular Sieves from Aqueous Solution

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Abstract

Industrial effluents discharged from dying industry is toxic for living organisms.Mesoporousaluminophosphate molecular sieve is synthesized and it is applied for the removal of Brilliant Green and Brilliant Yellow from aqueous solution. The adsorption studies are carried out at various experimental conditions like contact time, different initial dye concentrations, temperature, pH and adsorption dosage for finding the maximum adsorption. The contact time studies proved that the adsorption equilibrium attained at 20 minutes for the adsorption of BG and BY. The dye removal decreases with increased of dye concentration of BG and BY. The temperature study proved that the percentage removal of BY and BG on the adsorbent increases with increased of the temperature. The adsorbent dosage results are shown significant increase in the amount of dye removal due to increase the surface area and active sites of adsorbent. Since the negative ΔG value and positive ΔH value for the adsorption of BG and BY on adsorbent is 67.53KJmol^{-1} and 66.21KJmol^{-1}respectively. Desorption of dyes with ethanol and followed by calcination are carried out to regenerate the adsorbent.

Keywords : *Dye adsorption; Dye Desorption; Industrial effluents; Mesoporous Aluminophosphate.*

1. INTRODUCTION

Water plays an important role in the world economy, as it functions as a solvent for a wide variety of chemical substances and facilitates industrial cooling and transportation. Approximately 70% of the fresh water used by humans goes to agriculture [1].The most important water pollutants are metal ions, dissolved organic compounds and dyes[2]. Industrial effluents discharged from dying industries are highly coloured with large amount of suspended organic solid. These effluents are discharge into rivers make water unfit for domestic, agriculture and industrial purpose [3]. Many dyes and their break down products may be toxic for living organisms. It is estimated that about 10-15% dyes are realized into processing water during this procedure it is broadcasted that more than 60% of dyes world production is consumed by textile industries [4]. Dyes can be of many different structural varieties like acidic, basic, disperse, azo, anthraquinonebased and metal complex dyes among others. Dyes according to their structures, classified as anionic and cationic dyes[5]. In aqueous solution anionic dye carry a net negative charge due to the presence of amine or sulphur containing groups[6]. Several treatment processes are in practice for the removal of dyes from waste water. Adsorption is more efficient compared to conventional physico-chemical methods for the removal of organic wastes. The dye adsorbed adsorbent disposal also create environmental issues.To overcome all the issues, we are prepared a reusable adsorbent of $AlPO_4$. The $AlPO_4$ is used as an adsorbent for adsorption of dyes such as Brilliant Green and Brilliant Yellow.

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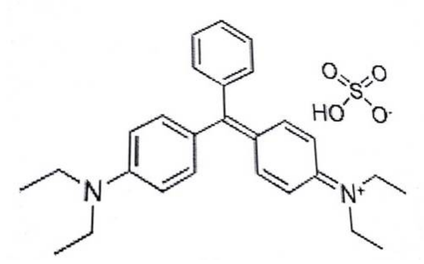
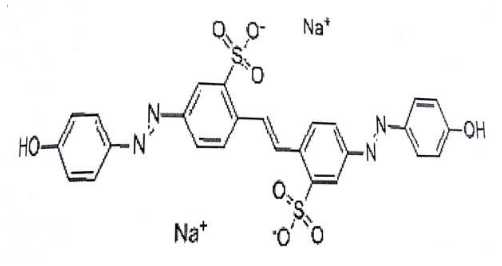
2. EXPERIMENTAL SECTION`

2.1 Materials

The chemicals used in the present work are pure analytical grade and used directly without further purification. The Cationic dye Brilliant Green (BG) and anionic dye Brilliant Yellow (BY) were used to study the hazardous dye removal. The properties of BG and BY are given in Table 1.

Table 1. Physical Properties of Dyes

Properties	BG	BY
Structure		
Molecular formula	$C_{27}H_{33}N_2HO_4S$	$C_{26}H_{18}N_4O_8Na_2S_2$
Molecular weight	482.64	624.55
Maximum adsorption λ_{max}(nm)	625	397

2.2 Synthesis of mesoporous $AlPO_4$

In a typical synthesis, 7.48g of aluminium hydroxide is added to the 17.5g of sodium dodecyl benzene sulphonate solution with vigorous stirring. Then 9.8g of phosphoric acid solution is added to the mixture . The mixture is stirred for 6 hours at room temperature. The final gel with a molar composition, Al_2O_3:P_2O_5:0.5SDBS:300H_2O is heated to 150°C with stiring up to the complete precipitation of the aluminophosphate mesoporous molecular sieves. The final product is washed repeatedly with distilled water, filtered and dried at 120°C for 3hours. This as-synthesized sample is calcined at 600°C for 6 hours to remove the template, organic contaminants and activate the active sites of mesoporous aluminophosphate molecular sieves.

2.3 Adsorption Experiment

The mesoporous $AlPO_4$is activated by heating in an electric Bunsen at 500°C for 4 hours to remove the physically adsorbed species present in the pores and the surface. Then the 0.5g of mesoporous $AlPO_4$is added with 50ml of BG and BY solutions separately. The solution is agitated at 150rpm. The solution concentration is measured by spectrophotometrically. To find out the maximum removal of BG and BY over mesoporous $AlPO_4$, the experimental conditions like contact time, different initial dye concentrations, temperature, pH and catalyst dosage are optimized. The effect of contact time is studied up to adsorption equilibrium time. The effect of pH was studied in the pH range from 2 to 10. The adsorption of BG and BY over mesoporous$AlPO_4$ isstudied in the concentration range of 100 – 500mg/L. The temperature effect of adsorption of BG and BY is studied in the range of 30°C-70°C. The mesoporous $AlPO_4$ dosage effect is studied in the range of 0.5 - 2.5g.

The adsorption capacity (mg dye/g adsorbent) of mesoporous $AlPO_4$is calculated by using the following equation,

$$q = (C_0 – C_e)\ V/W$$

The dye removal percentage (%) is calculated by using the following equation:

$$\text{Dye removal in percentage} = (C_0 – C_e) \times 100/ C_0$$

where, q is the amount of dye adsorbed on mesoporous $AlPO_4$ (mg/g), $C_0$and$C_e$are the initial and final dye concentrations in solution (mg/l), respectively. V is the volume of solution (L), and W is the adsorbent weight (g).

3. RESULT & DISCUSSION

3.1 FT-IR Characterization of MesoporousAlPO$_4$

To confirm the formation of tetrahedral framework of AlPO$_4$, FT-IR characterization has been carried out. The FT-IR of the calcined sample is shown Fig. 1.

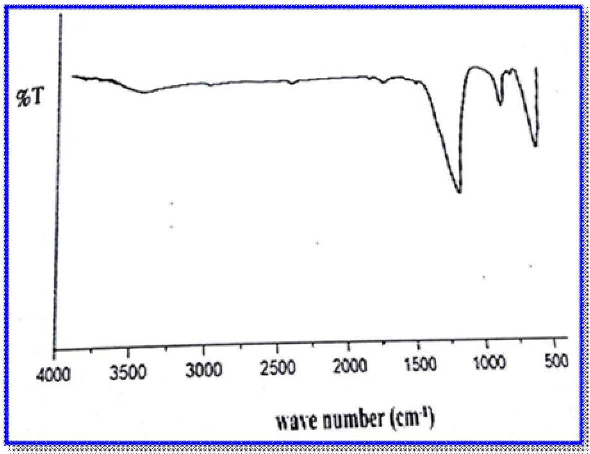


Fig. 1: FT-IR spectrum of calcined mesoporous AlPO$_4$

The asymmetric stretching of tetrahedral framework of AlPO$_4$is observed near 1106cm^{-1}and corresponding symmetric stretching is observed around 674cm^{-1}and bending mode is positioned near 466cm^{-1}. These vibrations confirm the formation of AlPO$_4$molecular sieves. The broad peak at 3423cm^{-1}is due to –OH groups and water molecules present in the molecular sieves.

3.2 Adsorption Studies

3.2.1 Effect of contact time

The effect of contact time has been studied at room temperature (30°C) for the adsorption of BG and BY on mesoporousAlPO$_4$upto 30 minutes (Fig. 2). The very rapid adsorption is observed at 20 minutes for both cationic and anionic dyes (BG &BY) and further increase of contact time not much increased the adsorption percentage. This is due to attain the adsorption equilibrium of BG and BY dyes on mesoporousAlPO$_4$molecular sieves. Both dyes structure and charge are different, but both are adsorbed rapidly. This indicated that the pore size and active sites are sufficient to accumulate different types of dye molecules.

3.2.2 Effect of pH

The effect of pH is studied in the pH range from 2 to 10 for the adsorption of dyes (Fig. 3). The pH of the solutions are adjusted by using 0.1N NaOH and/or 0.1N HCl. The adsorption of BG increased gradually with increase of pH and reach maximum at pH =10 and adsorption of BY decreased gradually with increase of pH =10. The low adsorption of BG at low pH may be due to repulsive force with the mesoporousaluminophosphate. Hence, the adsorption decreased in acidic pH. When pH increases above 7, the surface of the mesoporousaluminophosphate occupied negatively charge, and hence the adsorption of cationic dye BG increased and reached maximumat pH = 10 and the adsorption of anionic dye BY decreased. Because above pH 7, the surface of adsorbent becomes more basic, so it repels the anionic dye.

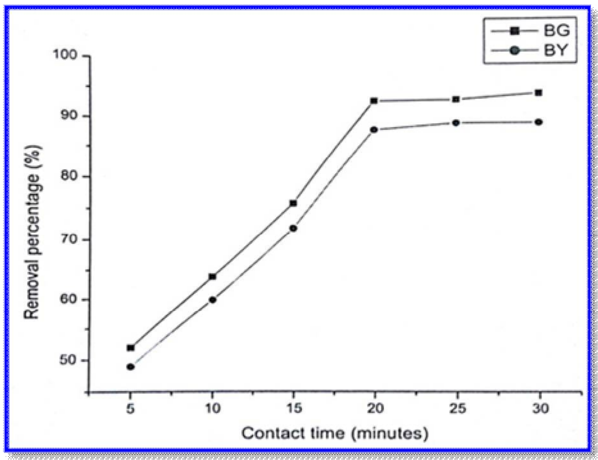


Fig. 2:. Effect of contact time for adsorption of BG and BY over mesoporous AlPO$_4$

Concentration : 100 mg/L, Temperature: 30°C, Adsorbent dosage: 0.5g

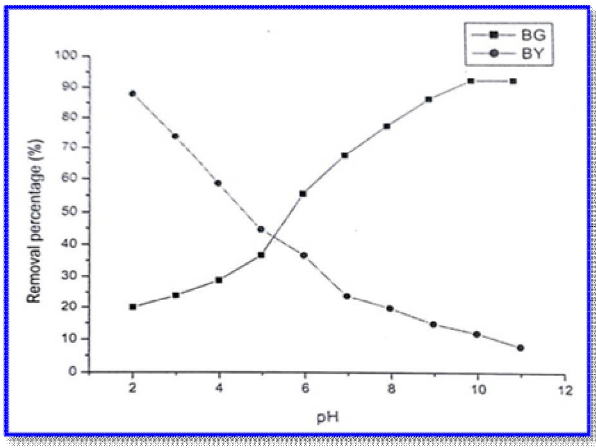


Fig. 3: Effect of pH for adsorption of BG and BY on mesoporous AlPO$_4$

Contact time:20mins,Concentration : 100 mg/L, Temperature: 30°C, Adsorbent dosage: 0.5g

3.2.3 Effect of Concentration

The BG and BY adsorption on mesoporous $AlPO_4$is studied between the concentrations range 100mg/L – 500mg/L at room temperature are shown in Figure 4. The adsorption capacity of the mesoporous $AlPO_4$is found to be maximum at 100mg/L and further increased of concentration decreased the adsorption of BG and BY on the adsorbent. The initial concentration provides an important driving force to overcome all mass transfer resistance of the dye molecule between the aqueous and solid phases. When increase the concentration of dye solution, the surface area and active sites are saturated and hence adsorption decreased with increase of dye concentration.

3.2.4 Effect of temperature

The effect of temperature for the removal of BG and BY on mesoporous $AlPO_4$are studied in the range of 303K to 343K is shown in the Figure 5. The adsorption increased with increase of temperature from 30°C to 70°C which indicated that the adsorption process is endothermic. This may due to increase of interaction between adsorbate and adsorbent.

3.2.5 Effect of adsorbent dosage

The effect of adsorbent dosage (0.5g – 2.5g) on adsorbent of BG and BY is studied (Figure 6). The percentage removal of the BG and BY is found to be increased with increase of adsorbent dosage. Since increased of adsorbent dosage increased the surface area and active sites. Hence, adsorption increased with increase of mesoporous $AlPO_4$ dosage.

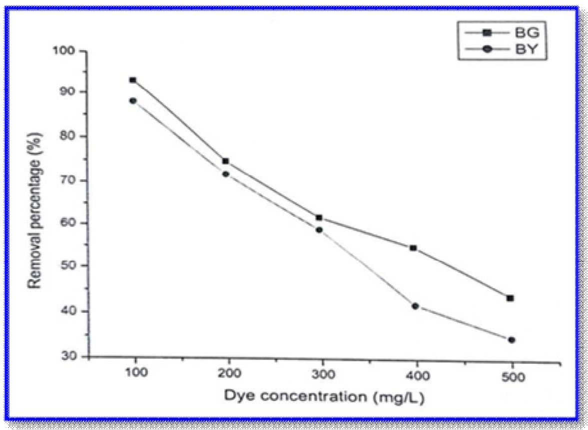


Fig. 4: Effect of concentration for adsorption of BG and BY on mesoporous $AlPO_4$

Contact time:20mins, Temperature: 30°C, Adsorbent dosage: 0.5g, pH :10

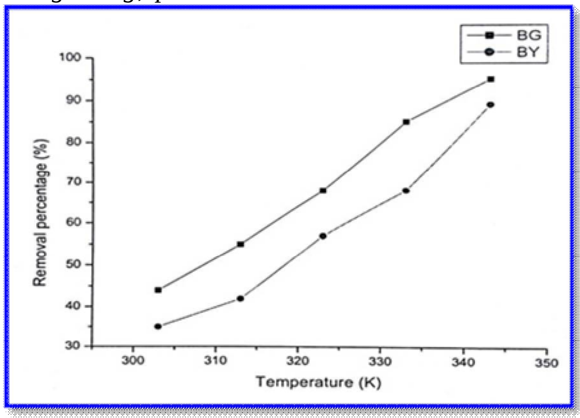


Fig. 5: Effect of temperature for adsorption of BG and BY on mesoporous $AlPO_4$

Contact time:20mins, Concentration : 100 mg/L, Adsorbent dosage: 0.5g,pH :10

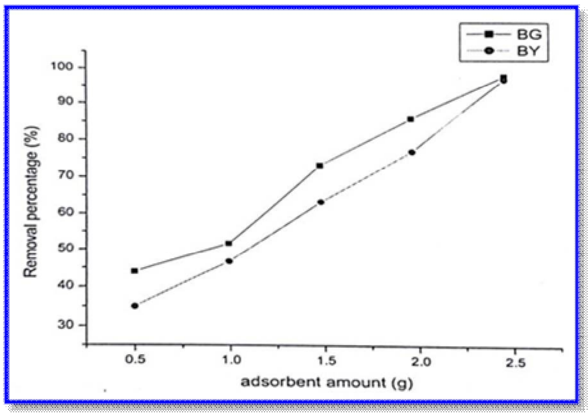


Fig. 6: Effect of adsorbent dosage for adsorption of BG and BY on mesoporous $AlPO_4$

Contact time:20mins, Concentration : 100 mg/L, Temperature:30°C,pH :10

3.3 Adsorption Isotherms

3.3.1 Langmuir adsorption Isotherms

The adsorption isotherm data at different concentration are measured and the data are given in the Table 2.

The Langmuir equation is represented as

$$C_e/Q_e = 1/Q_{max}\, K_L + C_e\, /Q_{max} \text{ ---- eq. 1.}$$

where,

Q_e is the equilibrium concentration of dye on the adsorbent (mg/g).
C_e is equilibrium concentration of dye in the solution (mg/L)

Q_{max} is the monolayer capacity of adsorbents (mg/g)

K_L is the Langmuir adsorption constant

The Langmuir constant K_L is a measure of affinity between adsorbent and adsorbate and $1/K_L$ value gives the half maximum adsorption. A plot of C_e/Q_eVsC$_e$ gave a straight line with slope $1/Q_{max}$ and intercept $1/Q_{max}$ K_L(Fig.7). The R^2 values for the adsorption of BG and BY on mesoporous $AlPO_4$ are given in the Table 2. The R^2 value is very close to 1 indicated that the adsorption obeys the Langmuir adsorption isotherm. The monolayer adsorption capacity of mesoporous $AlPO_4$ for BG is 23.69 mg/g and 8.02 mg/g for BY clearly indicated that the mesoporous $AlPO_4$ has more affinity with BG molecule than BY.

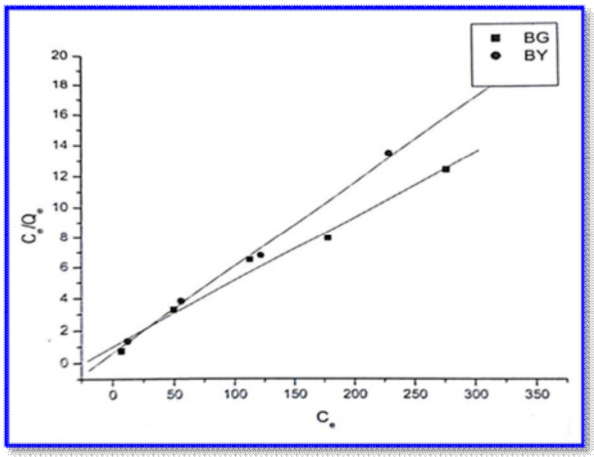


Fig. 7: Langmuir adsorption isotherms plot of BG and BY on mesoporous $AlPO_4$

3.3.2 Freundlich adsorption isotherm

The adsorption studies are carried out at various concentration and the adsorption values are applied to the Freundlich equation to verify the adsorption isotherms (Table 2). This study has been applied out as a model for understanding the multilayer adsorption of BG and BY on mesoporous $AlPO_4$.

The Freundlich equation is represented as,

$$\ln Q_e = \ln K_F + (1/n) \ln C_e \text{ ----- eq.2.}$$

where

K_F is the Freundlich constant
Q_e is the equilibrium concentration of dye on the adsorbent (mg/g)

C_e is equilibrium concentration of dye in the solution (mg/L)

1/n is the number of layers

The plot of $\ln Q_e$V$_s$$\ln C_e$ gave a straight line (Fig.8) with the intercept K_F and the slope 1/n.The R^2 values for adsorption isotherm of BG and BY are 0.994 and 0.938 respectively (close to 1) on mesoporous $AlPO_4$molecular sieves indicated that BG and BY adsorption followed the freundlich adsorption isotherm.

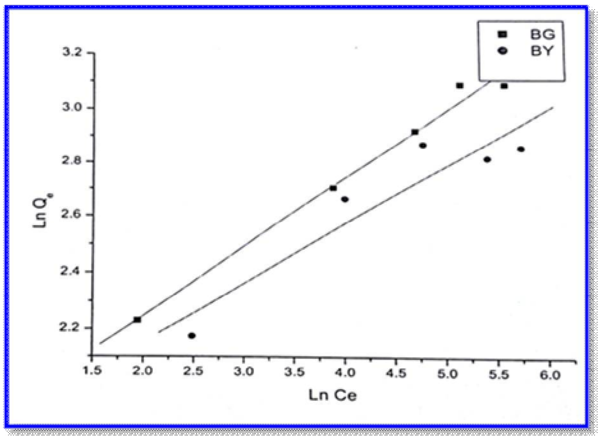


Fig. 8:Freundlich adsorption isotherms plot of BG and BY on mesoporous $AlPO_4$

Table 2. Langmuir and Freundlich adsorption isotherm parameters

Dye	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	R^2 Value	$1/Q_{max}$	K_L	R^2 value	n	K_F
BG	0.992	23.69	0.0420	0.994	3.92	0.5625
BY	0.999	18.02	0.0899	0.938	3.52	0.5499

3.4 Adsorption Kinetics

3.4.1 Pseudo second order kinetics

The adsorption kinetics of BG and BY on polythene powder is studied to find out the rate constant of the adsorption with regular time interval at room temperature. The experimental values are introduced in Pseudo second order kinetics equation for calculating rate constant.

The equation is represented as follows,

$t/Q_t = 1/k\ Q^2_e + 1/Q_e\ t$-----eq.3.

where

k is the rate constant

Q_e and Q_t are the amount of the dye adsorbed per unit mass of the adsorbent at equilibrium and t is time.

The plot of t/Q_tV_s t gives a straight line. Linear plot of t/Q_tV_s t is given in the Figure.9 for BG and BY adsorption on mesoporous$AlPO_4$. The linear regression coefficient is close to 1 (Table 3) indicated that the adsorption of BG and BY on mesoporous $AlPO_4$is fitted with the pseudo-second order kinetics .

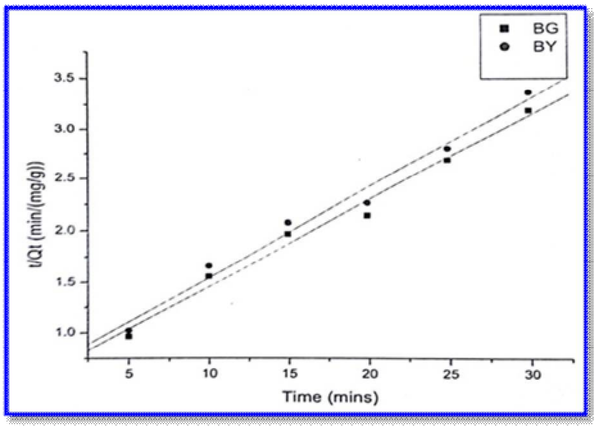


Fig. 9: Kinetics studies for the adsorption of BGand BY on mesoporous $AlPO_4$

Table 3. Pseudo second order kinetic parameters

Dyes	R^2 value	Pseudo second order rate constant (k)	Q_e (mg/g)
BG BY	0.991 0.990	0.0114 0.0115	11.904 11.386

3.5. Adsorption Thermodynamics

The thermodynamics parameters, namely free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have an important role to determine spontanenity and heat change for the adsorption process. The thermodynamic parameters are calculated using the following relations.

$$K_D = Q_e / C_e$$
$$\Delta G° = - RT \ln K_D$$
$$\ln K_D = (\Delta S / R) – (\Delta H / R)\ (1/T)$$

from the above equations,

$$\Delta G = \Delta H – T\Delta S$$

Where,

$K_D$is the distribution coefficient of the adsorbate, qe and Ce are the equilibrium dye concentration on mesoporous $AlPO_4$(mg/g) and in the solution (mg/L) respectively. R is the universal gas constant and T is the temperature (K). The enthalpy and Entropy can be calculated from the Van't Hoff plot as shown in the Figure.10 for BG and BY adsorption on mesoporous $AlPO_4$. The thermodynamics data are given in the Table 4.ΔG° values at the temperature of 303, 313, 323, 333, 343K are negative. This indicated that the process is feasible adsorption process and spontaneous. The enthalpy (ΔH°) values greater than 40K/J mol for both dyes (67.53 K/J mol for BG and 66.21 K/J mol for BY) indicated that the adsorption of BG and BY over mesoporous $AlPO_4$is chemisorption and BG is highly adsorbed than BY. The positive values of enthalpy indicated that the adsorption process is endothermic. Moreover, the positive values of ΔS° indicated that the degrees of freedom increased at the solid – liquid interface during the adsorption.

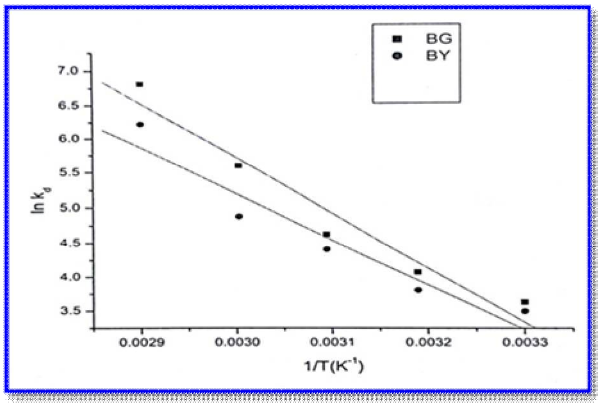


Fig..10: Adsorption thermodynamic plots of BG and BY on mesoporous $AlPO_4$

Table 4. Thermodynamics parameters for adsorption of BG and BY

S. No	Thermodynamic parameters	BG	BY
1.	ΔH° (K/J mol)	67.53	66.21
2.	ΔS° (K/J mol)	0.249	0.211
3.	ΔG° (K/J mol)		
	T = 303 K	-8.0238	-7.723
	T = 313 K	-10.407	-9.833
	T = 323 K	-13.26	-11.743
	T = 333 K	-16.520	-14.053
	T = 343 K	-17.877	-16.163
4.	R^2	0.988	0.990

4. DESORPTION

To understand the nature of adsorption of both dyes over mesoporous $AlPO_4$ molecular sieves, desorption study carried out in water, methanol and propanol at 30ºC. 1g of the dye adsorbed (BG and BY) mesoporous $AlPO_4$ taken in a 50ml reagent bottle separately for 1 hour at 150rpm. The solution is centrifuged and the percentage of BG & BY present in the solution is found out by spectrophotometrically. The BG and BY are recovered 99% and 99.5% respectively from the mesoporous $AlPO_4$. The percentage of BG and BY dyes desorption is very poor in water due to the dyes chemisorption on $AlPO_4$ .After desorption of dyes, the mesoporousaluminophosphate is calcined at 400ºC for 4 hours for regeneration and it can be reused for further application in the removal of dyes from aqueous solution.

5. CONCLUSION

Mesoporousaluminophosphate molecular sieve was synthesized successfully. These prepared mesoporous $AlPO_4$ is characterized by FT-IR. It was applied for the removal of Brilliant Green and Brilliant Yellow from aqueous solution.The adsorption of BG and BY over mesoporous $AlPO_4$ is chemisorption. By comparing these two dyes BG is highly adsorbed than BY. The Langmuir and Freundlich isotherms are proved that the adsorption is multilayer. The adsorption kinetics indicated that the process follows Pseudo second order. The thermodynamic studies showed that adsorption process is spontaneous and endothermic. The mesoporousaluminophosphateis regenerated by desorption of dyes with ethanol and followed by calcinations of adsorbent for reusing purpose. The recovery study proved that the $AlPO_4$ is reusable. The study concluded that the mesoporous $AlPO_4$ is suitable for the removal of hazardous cationic dye BG and anionic dye BY from dye effluent.

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